THE HYPOTHESIS OF THE OSCILLATING IONIC BOND

A THESIS

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the Faculty of the Graduate Division

By

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In Partial Fulfillment

of the Requirements for the Degree

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SUMMARY

A hypothesis on chemical bonding in molecules was developed and quantitatively tested on simple molecules. The molecules were those of methane, ethane, propane, benzene, ethylene, acetylene, carbon dioxide, water, hydrogen sulfide, ammonia and diborane.

The hypothesis was developed as an alternative to the covalent bond theory of bonding electron pairs. Such an alternative is desirable because the mathematics of the covalent bond theory is so difficult that only a few problems related to molecules have been solved. Also, the predictions of the covalent bond theory often disagree with the experimental facts of carbon-carbon bonds.

In chemical bonding in molecules it is generally accepted that the tendency is always toward forming filled electron shells. According to the hypothesis developed later in this paper, electrons will fill the shells in some of the atoms throughout the molecule, thus forming ions with alternating positive and negative charges. Then, the positive ions will exert an attraction on the outer shell electrons of the neighboring negative ions, but if the atoms of the molecule are from opposite ends of the period, such as sodium and chlorine are, the filled shells on the ions will remain unchanged. If, however, the atoms that

form a molecule are small and are from near the center of the period and the ions can obtain filled shells by either losing electrons or gaining electrons, it is postulated that the charges on the ions oscillate from positive to negative by the process of the ions' losing or gaining electrons in order to obtain filled electron shells. The restriction that the atoms be small is justified in the development of the hypothesis. In some molecules, it will be possible for all electron shells to be filled at both extremes of the oscillation of charges. It may be noted that the charge distribution throughout the molecules is fixed when the sign of the charge on only one ion is fixed.

The hypothesis was tested by performing and comparing two independent computations of the same quantity.

One calculation was made from electrostatics. The energy evolved when the ions, treated as point charges, are brought together to form the molecule was computed directly from the Coulomb potential energy equation. This energy is called the electrostatic energy.

The other calculation was made from thermochemistry. The energy evolved when the ions are brought together to form the molecule was computed indirectly from the Born-Haber thermochemical cycle. The energy computed in this way is called the thermochemical energy.

The thermochemical energies of methane and ammonia were about one per cent less than their respective electro-

static energies. The thermochemical energy of carbon dioxide was about three per cent less than the electrostatic energy. The thermochemical energy of diborane was about eight per cent less than the electrostatic energy. Two thermochemical energies of water were computed, one for $H_2^{+1}O^{-2}$ and one for $H_2^{-1}O^{+2}$. The average of the two thermochemical energies was about one per cent more than the electrostatic energy, although one thermochemical energy was about 13 per cent higher than the electrostatic energy. The average thermochemical energy of hydrogen sulfide was about 16 per cent higher than the electrostatic energy.

There is, as yet, no experimental value of the negative ionization energy of neutral carbon atoms, which, in the context of this study, is the energy needed to fill the shell of the neutral carbon atom so that the formed ion has a charge of minus four. It was possible to compute the negative ionization energy of carbon from several hydrocarbons by assuming that the computed electrostatic energy of each molecule is equal to its thermochemical energy. The hydrocarbon molecules from which the negative ionization energies were computed are methane, ethane, propane, benzene and ethylene. The average negative ionization energy computed from these molecules is 91.85 eV per carbon atom.

The substances, diamond excepted, were gaseous.

The test of the hypothesis revealed a satisfactory agreement between the electrostatic and thermochemical

energies. These results inspire confidence in the hypothesis of the oscillating ionic bond.

CHAPTER I

INTRODUCTION

In the science of chemistry a concept universally accepted is that of the chemical bond. Abstract in conception and lying beyond the reach of any attempts to isolate it, the concept of the chemical bond is nevertheless indispensable in accounting for the many properties of chemical substances. It has, in fact, been viewed as an invention that accounts for the experimental facts of chemistry. Although chemical bonds are usually classified as being either ionic, covalent, or metallic, there are, to be sure, transitions among these three kinds of bonds. A molecule, for example, may exhibit partly ionic properties as well as partly covalent properties. A solid may exhibit partly metallic properties as well as partly covalent properties.

The differences in ionic, covalent, and metallic bonds are easily enumerated, yet for all their differences there is one process common to them all. They are usually interpreted as results of electronic processes.

The ionic bond is formed when the metal atom loses electrons and the non-metal atom gains electrons. The ions thus formed have filled electron shells.

The covalent bond is formed when pairs of electrons

are shared between neighboring atoms. The number of electron pairs is sufficient to create filled electron shells in all the atoms in the molecule by means of electron sharing.

Because the properties of metals are usually accounted for by the energy band theory and the electron gas theory, the metallic bond appears to be more complicated than either the ionic or the covalent bond. One important result derived from these complex theories is that the electrons are able to move in any direction in the lattice except for the restrictions imposed on them by the Brillouin zones and the boundaries of the metallic lattice.

The ionic, covalent, and metallic bond models have been used as a basis for computing bonding energies of the substances in which these kinds of bonding dominate. In ionic bonding, the bonding energies are computed from simple electrostatics, and, because the mathematics of such calculations is simple, the bonding energies of many ionic crystals have been successfully computed. In covalent and metallic bonding, however, the bonding energies of substances possessing such bonds are computed from quantum mechanics, and, in spite of thirty years of effort, the computed bonding energies of only a few substances have been reported. The bonding energies of two covalent bonded molecules, the hydrogen molecule and the hydrogen molecule ion, have been successfully computed. The bonding energies of two metals, lithium and sodium, have also been successfully computed.

This paper presents a new hypothesis on an electronic process in chemical bonding in molecules. The main features of the process are a tendency toward filled electron shells which causes ion formation, alternating charges between bonded ions, and a possibility of oscillation of the signs of the charges on small ions. The similarity of some of its features with those of existing theories will be easily recognized.

On the basis of the hypothesis, quantitative computations of the electrostatic energies of molecules can be made. The hypothesis can be tested by comparing the electrostatic energy with the thermochemical energy of the same molecule.

CHAPTER II

HISTORICAL DEVELOPMENT

In 1887 S. Arrhenius (1) published the theory of ionization of electrolytes in aqueous solution. The theory was widely accepted within two years although an important piece of the puzzle of ions remained missing until the discovery of the electron by J. J. Thomson in 1897. This discovery made possible Bohr's atomic model and from this theory the idea of the filled electron shell in ions. In 1916, G. N. Lewis (13), recognizing the stability of the filled electron shell, introduced the concept of the covalent bond in non-electrolytes. The covalent bond is assumed to be formed by common electron pairs. Both electrons in the bonding pair belong to the electronic shells of the bonded neighboring atoms. The number of electron pairs shared between neighboring atoms is adjusted until all the atoms in the molecule obtain filled electron shells. The concept of the covalent bond has been broadened and enriched by quantum mechanics, developed independently by Heisenberg (7) in 1925 and Schrödinger (21) in 1926. The ideas of resonance and bond orbitals, arising from quantum mechanics, appear to be firmly entrenched in the modern theories of structural chemistry.

The theory that the metallic bond is largely quantum mechanical dates from the development of quantum mechanics. Treatments of the theory may be found in the books by Seitz (22), Pauling (17), Mott and Jones (16), and others.

The first attempt to compute bonding energies was made in 1918 by Madelung (14), who devised a method for computing the binding energy of ionic crystals from electrostatics. Born (2) and Haber (6) in 1919 developed a method of computing the binding energy of ionic crystals from thermochemical data and ionization energies. By an application of Hess's assumption that the equations of chemical reactions may be treated as algebraic equations, they devised the thermochemical cycle that bears their names. Hylleraas (8) in 1931 and Jaffe (9) in 1934 computed the dissociation energy of the hydrogen molecule ion in complete agreement with experiment. James and Coolidge (10) in 1933 computed the energy of dissociation of the hydrogen molecule to within 0.03 eV of what they call the most probable experimental value.

A calculation of a different kind was made in 1941 by Price (20), who applied electrostatics to the problem of the orientation phenomenon in benzene. He demonstrated a correlation between certain electrostatic forces and the amount of meta orientation and concluded that the electrostatic explanation of orientation is superior to the resonance explanation.

As can be seen, the calculations of bonding energies have been approached both from the electrostatic and the quantum mechanical viewpoint. In spite of the lack of appreciation of the electrostatic approach, this method has yielded a greater variety of applications with excellent results than have the quantum mechanical calculations.

CHAPTER III

DEVELOPMENT OF THE HYPOTHESIS

Because the mathematics of the metallic bond theories and the covalent bond theories in the wave mechanical approach is so complicated, only a few calculations of the bonding energies of metals and covalent compounds have been made. In addition to mathematical difficulties, the results and predictions of the quantum mechanical theories of metallic bonding and covalent bonding are often in disagreement with experimental facts.

One example of such disagreement is in the properties of copper and zinc. According to the quantum mechanical theory, copper has one bonding electron per atom while zinc has two bonding electrons per atom. Yet, copper with one bonding electron has a higher melting point, greater Young's modulus, greater electrical conductivity, etc., than zinc with two bonding electrons.

Another example of disagreement of quantum mechanics with experimental facts is in the lengths of carbon-carbon double bonds. The carbon-carbon double bond in ethylene is accounted for by the use of π and σ bonding electrons. The carbon-carbon double bond is supposed to be formed by the overlap of the two π electron orbitals with the σ electron

orbitals perpendicular to the direction of the π electron orbitals. Moreover, the σ electron orbitals are supposed to attract each other, thus shortening the carbon-carbon double bond in ethylene. If the idea of π and σ electron orbitals is applied to carbon-carbon double bonds in longer chain hydrocarbons such as butadiene, the lengths of the double bonds should be expected to be at least as short or shorter than the double bond in ethylene, due to the electron attraction. Yet, the carbon-carbon double bond in butadiene is nearly an Angstrom unit greater than that of ethylene.

The mathematical difficulties and the qualitative disagreement of quantum mechanics with experimental facts indicate that a better theory is needed and desired. Since the electrostatic approach has been so successful in computing bonding energies, the possibility of substituting, in some cases, the ionic concept for covalent and metallic bonding will be explored.

The hypothesis is developed from the consideration of certain experimental facts.

Engel (5) has observed a regular pattern in the energies of atomization of the elements in each period. In the second period, for example, lithium and fluorine have almost the same energies of atomization. Beryllium and oxygen have almost the same energies of atomization, but the energies

are higher than those of lithium and fluorine. Boron and nitrogen have almost the same energies of atomization and carbon has the highest energy of all. The increase of energies from lithium to carbon is roughly linear. The decrease of energies from carbon to fluorine is also roughly linear. In the third period the pattern is similar but the energies are lower. These relations for the second period are shown in Figure 1.

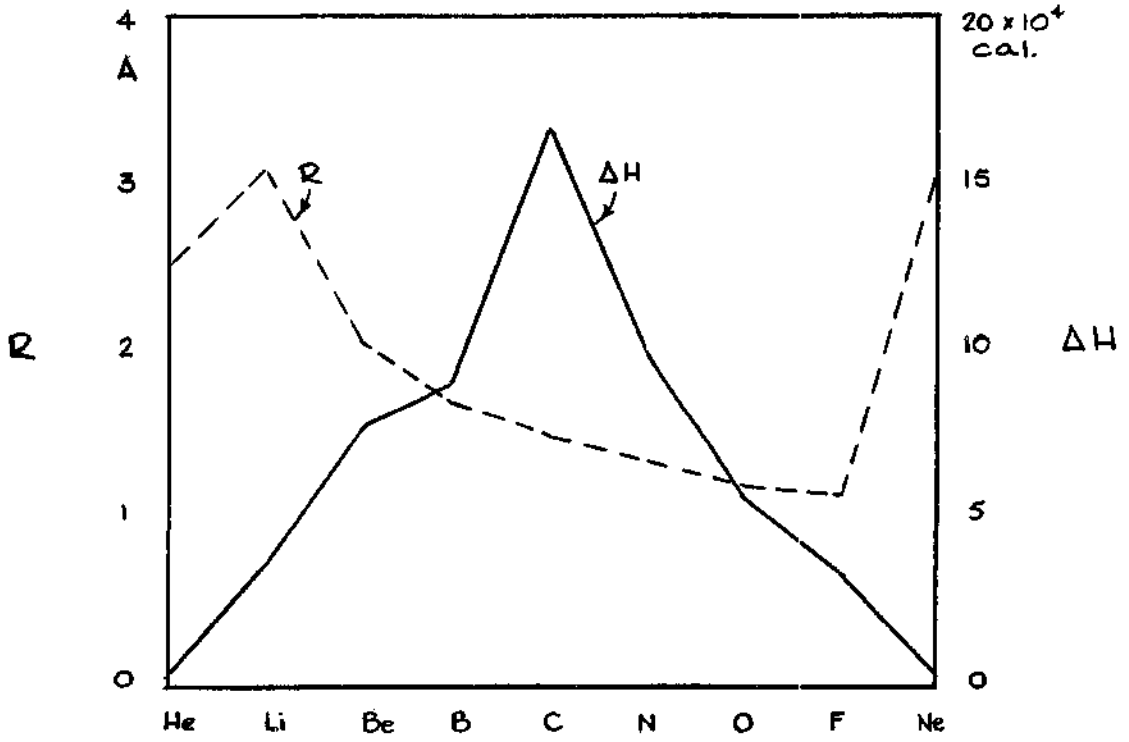


Figure 1

Representation of the Energies of Atomization, ΔH, and the Interatomic Distances, R, of the Pure Elements in the Second Period.

The atomic distances of the elements have little if any influence on their energies of atomization. Engel (5) has pointed out that the energies of atomization depend on the number of bonding electrons per atom in agreement with Lewis's electron pair theory. That is to say, lithium and fluorine have one bonding electron pair each, beryllium and oxygen have two bonding electron pairs each, and so on. It is generally accepted that each atom has a fixed and well defined pattern of quantum states and Engel postulates that these quantum states are essentially unchangeable. Electrons may jump from one quantum state to another as they do in light absorption and emission phenomena, and they may remain in excited states if bonding conditions demand it. When atoms enter into chemical compounds, the quantum states remain the same. The occupation of the quantum states in the atom may change, although the pattern of the quantum states remains fixed. Engel points out that beryllium, boron and carbon in the solid state must be assumed to have different electron configurations than those determined spectroscopically from beryllium, boron and carbon in the monatomic gaseous state. The electron configuration and the number of bonding electrons as required to explain the fact of atomization energies according to the electron pair theory are shown for the second period in Table 1. The same number of bonding electrons is obtained for the third period.

Table 1

Electron Configurations and
Bonding Electrons in the Second Period

Element	1 s	2 s	2 p	Bonding Electrons
Li	2	1		1
Be	2	1	1	2
B	2	1	2	3
C	2	1	3	4
N	2	2	3	3
O	2	2	4	2
F	2	2	5	1

There is another way to account for the experimental facts. The bond between pairs of atoms in the second period is assumed to be formed in a special way. The pairs form ions when electrons are transferred from one atom to the other. If enough electrons are transferred so that one of the ions has a filled shell, a pattern identical to the number of bonding electrons per atom is obtained. One electron is transferred in the lithium pair, two electrons are transferred in the beryllium pair, three electrons are transferred in the boron pair, and so on. The results are shown in Table 2.

Table 2

A Correlation between Energies of Atomization and Number of Transferred Electrons to Fill Shell

Atomic Pair	Electrons transferred	Charges
Li-Li	1	Li^{+1}-Li^{-1}
Be-Be	2	Be^{+2}-Be^{-2}
B-B	3	B^{+3}-B^{-3}
C-C	4	C^{+4}-C^{-4}
N-N	3	N^{+3}-N^{-3}
O-O	2	O^{+2}-O^{-2}
F-F	1	F^{+1}-F^{-1}

The number of electrons transferred per pair of atoms is directly related to the pattern of the energies of atomization. It should be noted that although both beryllium ions, both carbon ions, and both nitrogen ions have filled shells, only one ion in each of the other pairs has a filled shell.

Since the tendency in chemical bonding in molecules is toward filled shells, the consequence is that some electrons will leave the shells of their atoms and enter quantum states in the shells of neighboring atoms. This migration of electrons will form ions and thus cause the signs

of the charges to alternate throughout the molecule. The atoms stripped of their outer shell electrons form positive ions. Some ionic molecules, such as sodium chloride, can have filled shells only if sodium loses an electron and chlorine gains an electron. If the charges in sodium chloride were reversed, neither sodium nor chlorine would have filled shells. The situation is different in a pair of lithium ions such as given in Table 3. Even when the charges on the lithium ions are reversed, there is still a stripped lithium ion with a filled shell. It seems possible that the charges on the lithium ions could oscillate from positive to negative due to the attraction of the positive lithium ion on the outer shell electrons of the negative lithium ion. The ionic bond, being distance dependent, may dominate in molecules if the atoms are small. If the atoms forming a molecule are small and come from near the middle of the period so that filled shells may be formed by a nearly equal loss or gain of electrons, the bonds may be ionic and the charges on the ions may oscillate.

The hypothesis of this study may be stated.The tendency in chemical bonding in molecules toward filled electron shells will cause electrons to leave the shells of certain atoms and seek the shells of neighboring atoms, thus forming ions with alternating positive and negative charges. Since the ionic bond is distance dependent, it may dominate

over covalent bonding among small atoms. If the atoms are from near the center of the period so that a nearly equal loss or gain of electrons will form filled shells, the charges on the ions may oscillate.

The ideas presented in the hypothesis suggest that it be called the hypothesis of the oscillating ionic bond.

CHAPTER IV

METHODS OF CALCULATION

In testing the hypothesis, computations were made on twelve substances: methane, ethane,propane, benzene,ethylene, acetylene, carbon dioxide, water, hydrogen sulfide, ammonia, diborane, and diamond. These substances were chosen because of their simple molecular structure and because thermochemical data and bond data are available for them.

The term "electrostatic energy," as used in the context of this paper, denotes the energy evolved when ions, treated as point charges, are brought together from a great distance to form the molecule. The units of electrostatic energy are in electron volts per molecule. The electrostatic energies were computed directly from the Coulomb potential energy equation with the exception of the bonding in the diamond lattice. Madelung's constant was used in conjunction with the Coulomb potential energy equation to compute the electrostatic energy of the diamond lattice. The electrostatic energy remains unchanged when the signs of the ionic charges are reversed in the oscillating ionic bond.

No correction was made for the repulsion between outer electron shells.

The term "thermochemical energy," as used in the context of this paper, denotes the energy evolved when ions with filled shells are brought together from infinity to form a molecule. This energy is calculated indirectly by use of the Born-Haber thermochemical cycle. The units are in electron volts per molecule. The thermochemical energy, unlike electrostatic energy, may be changed if the ionic charges are reversed because of the different ionization energies of positive or negative ions.

The negative ionization energy of carbon is not available from experiment but it was possible to compute it from methane, ethane, propane, benzene, and ethylene. In these calculations the electrostatic energy was substituted for the thermochemical energy, the negative ionization energy was computed, and the average negative ionization energy of these five molecules was taken as the negative ionization energy of carbon.

The experimental data used in the electrostatic calculations were bond lengths and bond angles.

The experimental data used in the thermochemical calculations were energies of formation of molecules, energies of atomization of the elements, energies of dissociation of diatomic molecules, positive ionization energies of the elements, and negative ionization energies of the elements. The negative ionization energies were available for hydrogen, oxygen, and sulfur.

CHAPTER V

DETAILS OF CALCULATIONS

To illustrate the methods of computation, the electrostatic energy and the thermochemical energy of methane will be computed. The carbon ion is assumed to have a charge of plus four.

Methane is depicted below:

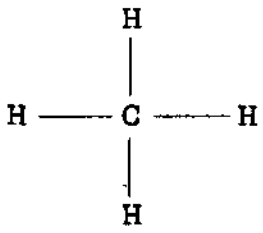


Figure 2. Methane.

The bond lengths and bond angles for methane are:

$$C\text{-}H = 1.091 \text{ A}$$

$$H\text{-}H = 1.782 \text{ A}$$

$$< HCH = 109.5^{o}$$

The computation of electrostatic energy follows:

Table 3

Electrostatic Energy of Methane

Ions	n	Q_1Q_2	nQ_1Q_2	R	$nQ_1Q_2R^{-1}$
C-H	4	-4	-16	1.091	-14.6654
H-H	6	+1	+ 6	1.782	+ 3.3670

$$\Sigma nQ_1Q_2R^{-1} = -11.2984$$

$$\Delta E = (14.398)(-11.2984)$$

$$\Delta E = -162.67 \text{ eV}.$$

The ions between which the electrostatic energy is calculated are represented in the first column and the number of such pairs of ions is denoted by n. There are four pairs of C-H type ions in methane. The product of the charges is denoted by Q_1Q_2. Q_1 is the charge on the first ion and Q_2 is the charge on the second ion. The distance between a pair of ions is denoted by R. The expression $nQ_1Q_2R^{-1}$ is derived from n, Q_1Q_2, and R. The electrostatic energy is represented by ΔE.

The constant in the Coulomb potential energy equation is chosen so that ΔE is in electron volts when R is in Angstrom units and Q_1 and Q_2 have integral units of charge such as 1, 2, 3, . . . Its value is 14.398.

CHAPTER VI

RESULTS AND DISCUSSION

The comparison between the electrostatic energies and the thermochemical energies is shown in Table 4 on the following page. The units are in electron volts per molecule. Note that the charges on the carbon ions in benzene alternate from plus four to minus four. The sign of the charge of the attached hydrogen is opposite to that of the carbon.

The electrostatic energy of a bonded pair of carbon ions inside the diamond lattice was computed by multiplying the electrostatic energy of the two carbon ions by the Madelung constant. The Madelung constant for sphalerite, a variety of zinc blende, is reported by Pauling (17). Because the lattice structures of sphalerite and diamond are identical, Madelung's constant for sphalerite may be used in computing the electrostatic energy of the bonded C-C pair of ions in diamond. The designation of the pair of carbon ions in the diamond lattice as a "molecule" is one of convenience.

The quantity $\frac{\Delta E - \Delta H}{\Delta E} x100$ is denoted by P.

Table 4

Comparison of Electrostatic Energies with Thermochemical Energies

Molecules	Charges	ΔE	ΔH	P
CH_4	$C^{+4}H_4^{-1}$	-162.67	-160.90	+ 1.09
CH_4	$C^{-4}H_4^{+1}$	-162.67	-162.05	+ 0.38
C_2H_6	$C^{-4}H_3^{+1}C^{+4}H_3^{-1}$	-304.72	-304.87	- 0.05
C_3H_8	$C^{-4}H_3^{+1}C^{+4}H_2^{-1}C^{-4}H_3^{+1}$	-450.57	-448.94	+ 0.36
C_3H_8	$C^{+4}H_3^{-1}C^{-4}H_2^{+1}C^{+4}H_3^{-1}$	-450.57	-447.79	+ 0.62
C_6H_6		-809.64	-806.71	+ 0.36
C_2H_4	$C^{-4}H_2^{+1}C^{+4}H_2^{-2}$	-281.71	-286.05	- 1.54
C_2H_2	$C^{-4}H^{+1}C^{+4}H^{-1}$	-253.81	-266.84	- 5.13
CO_2	$C^{-4}O_2^{+2}$	-173.32	-204.56	-18.02
CO_2	$C^{+4}O_2^{-2}$	-173.32	-177.73	- 2.54
C-C	$C^{-4}C^{+4}$	-244.23	-251.75	- 3.08
H_2O	$H_2^{+1}O^{-2}$	- 50.62	- 44.08	+12.92
H_2O	$H_2^{-1}O^{+2}$	- 50.62	- 56.92	-12.45
H_2S	$H_2^{+1}S^{-2}$	- 35.43	- 41.84	-18.09
H_2S	$H_2^{-1}S^{+2}$	- 35.43	- 39.92	-12.67
B_2H_6	$B_2^{+3}H_6^{-1}$	-174.07	-160.07	+ 8.04
NH_3	$N^{+3}H_3^{-1}$	-101.94	-100.38	+ 1.53

The reliability of the experimental data is examined to demonstrate the degree of reliability of the calculated results.

Some error is present in the energies of formation of molecules as determined from calorimetric measurements of energies of combustion. Any error in the energy of combustion makes a greater error in the energy of formation. Daniels and Alberty (4) illustrate this magnification of error in the case of n-butane. An error of 0.2 per cent in the energy of combustion of n-butane introduces an error of 4.7 per cent in its energy of formation. For most molecules the energies of formation are about one electron volt per molecule and any error as large as, say, ten per cent in the energy of formation will contribute no significant error to the calculated results in this study, because the magnitudes of electrostatic and thermochemical energies are much larger than one electron volt.

The energies of atomization of boron, carbon, and sulfur are about five times greater than most of the energies of formation of molecules used in this paper. The values reported in the literature vary. Cottrell (3) has reviewed the energies of atomization of the elements and, in most cases, recommends what he thinks is the best value. His recommendations have been followed in this study.

The table below shows the extreme values of the

energies of atomization of boron, carbon, and sulfur, as well as the recommended values:

Table 5

Energies of Atomization
of Elements in the Solid State
in Electron Volts per Atom at 25°C

Element	High Value	Low Value	Recommended
B(s)	6.50	4.21	-
C(s)	7.40	4.76	5.98
S(s)	2.87	2.31	2.87

C(s) denotes graphite and S(s) denotes rhombic sulfur. Cottrell recommended no value for the energy of atomization of boron because the boiling point of elementary boron is uncertain and because pure boron is difficult to obtain. Cottrell reports that the value of 4.21 eV is suggested by the National Bureau of Standards. It is the value that was used in this study.

Table 6 on the following page shows the energies of atomization of molecular hydrogen, oxygen, and nitrogen. These values are recommended by Cottrell.

Table 6

Energies of Atomization of Diatomic Molecules in Electron Volts per Molecule Corrected to 25°C

Molecule	Energy of Atomization
$H_2(g)$	4.52
$N_2(g)$	7.42
$O_2(g)$	5.13

According to Cottrell (3), no energy of atomization of diatomic hydrogen has been reported in disagreement with 4.52 eV. Depending on the interpretation of spectroscopic data, 7.38 eV and 9.76 eV may both be obtained as the atomization energy of diatomic nitrogen. Electron impact methods yield 7.38 eV and, for this reason, Cottrell recommends 7.38 eV. The energy of atomization of diatomic oxygen has an unambiguous value of 5.13 eV, according to Cottrell.

The positive ionization energies used in this work are those compiled by Charlotte Moore (15) of the National Bureau of Standards. An indication of the accuracy of the positive ionization energies may be gained by noting that they are usually reported to three figures beyond the decimal.

The following table shows the energies in electron volts per atom required to negatively ionize hydrogen,

oxygen, and sulfur so that the shells are filled:

Table 7

Negative Ionization Energies of Monatomic Gases in Electron Volts per Atom

Negative Ion	Negative Ionization Energy
$H^{-1}(g)$	-0.72
$O^{-2}(g)$	+7.28
$S^{-2}(g)$	+3.44

The value of -0.72 was computed by Hylleraas (8) and is reported by Pitzer (19). No experimental values are available for $H^{-1}(g)$. Sherman (23) reports a value of 7.28 eV for oxygen and a value of 3.44 eV for sulfur. These values were computed from the Born-Haber thermochemical cycle. No direct measurements of these quantities have been reported. The negative ionization energy of carbon was computed by the writer.

The bond lengths and bond angles used in this paper were compiled by Sutton (24). The reliability that may be expected in bond lengths is discussed by Pauling (17). The most reliable bond lengths may be accurate to 0.001 A, and the less reliable bond lengths may be accurate to only 0.1 or 0.2 A. The degree to which such errors may affect the

calculated electrostatic energy is illustrated in the case of carbon dioxide. The carbon-oxygen distance is reported as 1.162 $\pm$ 0.010 Angstrom units. The writer computed the electrostatic energy of carbon dioxide and took this error into account. By using bond distances of 1.152 and 1.172, the corresponding electrostatic energies were computed to be -174.82 and -171.84 eV.

The repulsion due to the electron shells and to the molecular conformations of ethane and propane were omitted from the calculations. Except for diatomic molecules and some solids, the energy of repulsion is difficult to evaluate. An idea as to how much difference the repulsion makes may be gained from examining the computations of the electrostatic energy of sodium chloride. The writer computed the electrostatic energy of solid sodium chloride by using the Born-Haber cycle and Madelung's constant. When the repulsion of electron shells was taken into account, as prescribed by Pauling (17), the agreement between experiment and calculation was excellent. When the repulsion was not taken into account, the calculated value was about 14 per cent higher than the experimental value.

Because of internal rotation about a carbon-carbon single bond, ethane and propane have more than one arrangement of their atoms. Ethane may have its hydrogens in staggered or eclipsed conformation. In this study, only the

eclipsed conformations were chosen. Kemp and Pitzer (11) report a calculated difference of 0.26 eV between the staggered and eclipsed conformations of ethane.

Table 8 summarizes the estimated errors in the experimental data except for the errors in bond lengths given in Table 14, p. 36.

Table 8

Estimated Errors in Experimental Data

Atom	Energy of Atomization	Positive Ionization Energy	Negative Ionization Energy
Boron	± 0.70 eV	± 0.00 eV	
Carbon	± 1.30 eV	± 0.00 eV	± 3.56 eV
Sulfur	± 0.30 eV	± 0.10 eV	± 0.20 eV
Hydrogen	± 0.00 eV	± 0.00 eV	± 0.00 eV
Oxygen	± 0.00 eV	± 0.00 eV	± 0.40 eV
Nitrogen	± 0.00 eV	± 0.00 eV	

CHAPTER VII

A COMPARISON BETWEEN RESONANCE THEORY AND THE OSCILLATING IONIC BOND HYPOTHESIS

A thorough comparison of the resonance theory with the oscillating ionic bond hypothesis lies beyond the scope of this paper, but a brief comparison of a few features of each concept will be given.

An outstanding property of the resonance theory is a flexibility that allows it to be applied to a great variety of molecules. Although the mechanism of resonance is difficult to visualize, it accounts for the directional properties of certain chemical bonds. The mathematics associated with resonance, however, is so difficult that the computation of the binding energies of molecules other than those previously noted has not yet been made. It is generally accepted that the resonance theory attempts to reconcile experimental facts with the bond orbital concept. The bonds are supposed to be formed by overlapping bond orbitals. The bonds between atoms are supposed to be the shortest when there is the greatest number of overlapping bond orbitals between the atoms. This notion is inconsistent with electrostatics and does not account for the bond lengths in ethylene, benzene, styrene, diphenyl, graphite, and many other

organic molecules. Consequently, the additional theory of the π and σ electrons of carbon-carbon double bonds has been added. Yet, this auxilliary theory does not account for the bond lengths in the molecules mentioned above.

In contrast with resonance theory, which may be applied to molecules formed of atoms throughout the periodic table, the oscillating ionic bond hypothesis was developed especially for application to molecules formed of atoms from the first and second periods. Whether it can be extended to other periods is not yet known. The mechanism associated with the oscillating ionic bond is unambiguous and easily visualized. The bonds themselves no longer have directional properties as they have in resonance theory, but the molecular structures are easily accounted for by electrostatics. Because the mechanism of the oscillating ionic bond hypothesis is simple, the mathematics associated with it is simple, and, therefore, the bonding energies are easily computed. Moreover, the prediction in bond lengths by the oscillating ionic bond hypothesis is qualitatively correct. The structures of nearly all molecules appearing in this paper are consistent with the hypothesis, although the structures of water, hydrogen sulfide, and ammonia cannot be accounted for by the present form of the hypothesis.

CHAPTER VIII

CONCLUSIONS

The hypothesis of the oscillating ionic bond has been tested by comparing the electrostatic energies of molecules with their thermochemical energies with fairly good agreement. Although the test was made on the basis of independently computed energies, it is possible to test the hypothesis by other methods. For example, it could be tested for its consistency with the existing data of dipole moments and magnetic properties. Also, the comparison of electrostatic energies and thermochemical energies could be extended to molecules other than those that were used in this study. The hypothesis is worthy of such further study as indicated by the close agreement between the two independently computed energies.

A P P E N D I C E S

APPENDIX A

CONVERSION FACTORS AND DERIVATION OF THE ELECTROSTATIC ENERGY EQUATION

(1) Derivation of the Expression for the Electrostatic Energy between Two Point Charges.--The electrostatic potential energy released when two point charges are brought together from an initial separation of infinity to a final separation of R may be expressed as

$$\Delta E = -\int_{\infty}^{R} F dr \qquad (1)$$

where F represents the force between the two charges Q_1 and Q_2 separated by a distance r and is given by Coulomb's law:

$$F = kQ_1Q_2r^{-2} \qquad (2)$$

The minus sign is placed before the integral to make the sign of the electrostatic energy consistent with the sign conventions of thermochemistry.

After inserting the expression for F into equation (1) and integrating, the electrostatic energy becomes

$$\Delta E = kQ_1Q_2R^{-1} .$$

(2) Conversion of the Constant in the Electrostatic Potential Energy Equation.--According to Leighton (12), the constant k has a value of

$$8.98742 \times 10^{9} \text{ joule} \cdot \text{meter} \cdot \text{coulomb}^{-2} .$$

$$1 \text{ electron charge} = 1.60206 \times 10^{-19} \text{ coulombs.}$$

$$1 \text{ eV} = 1.60206 \times 10^{-19} \text{ joules.}$$

$$k = 8.98742 \times 10^{9} \frac{\text{joule} \cdot \text{meter}}{(\text{coulomb})^2} \times \frac{10^{10} \text{ A}}{\text{meter}} \times$$

$$\frac{(1.60206 \times 10^{-19} \text{ coulomb})^2}{(\text{electron charge})^2} \times \frac{\text{eV}}{1.60206 \times 10^{-19} \text{joule}} .$$

$$k = 14.3983 \frac{\text{eV} \cdot \text{A}}{(\text{electron charge})^2} .$$

(3) Conversion Factor for Converting Kilocalories per Mole to Electron Volts per Molecule:

$$1 \text{ eV molecule}^{-1} = 23.063 \text{ kcal mole}^{-1} .$$

Source: Cottrell (3), p. 3.

APPENDIX B

EXPERIMENTAL DATA

Table 9

Energies of Formation
in Electron Volts per Molecule at 25°C

Molecule	Energy of Formation
$CH_4(g)$	-0.78
$CH_3CH_3(g)$	-0.88
$CH_2CH_2(g)$	+0.54
$C_2H_2(g)$	+2.35
$C_6H_6(g)$	+0.86
$C_3H_8(g)$	-1.08
$CO_2(g)$	-4.08
$B_2H_6(g)$	+0.33
$H_2S(g)$	-0.21
$NH_3(g)$	-0.48
$H_2O(g)$	-2.51
C (diamond)	+0.04

Source: Perry (18), p.236 .

Table 10

Energies of Atomization of Elements
in the Solid State in Electron Volts per Atom at 25°C

Element	Energy of Atomization
B(s)	+4.21
C(s)	+5.98
S(s)	+2.87

Source: Cottrell (3), p. 154.

Table 11

Energies of Atomization of Diatomic Molecules
in Electron Volts per Molecule Corrected to 25°C

Molecule	Energy of Atomization
$H_2(g)$	+4.52
$N_2(g)$	+7.42
$O_2(g)$	+5.13

Source: Cottrell (3), p. 154.

Table 12

Positive Ionization Energies
of Monatomic Gases in Electron Volts per Atom

Atom	Final Charge	Positive Ionization Energy
H(g)	H^{+1}	+ 13.60
B(g)	B^{+3}	+ 71.37
C(g)	C^{+4}	+147.98
N(g)	N^{+3}	+ 91.57
O(g)	O^{+2}	+ 48.76
S(g)	S^{+2}	+ 33.76

Source: Moore (15).

Table 13

Negative Ionization Energies
of Monatomic Gases in Electron Volts per Atom

Atom	Final Charge	Negative Ionization Energy
H(g)	H^{-1}	- 0.72
C(g)	C^{-4}	+91.85
O(g)	O^{-2}	+ 7.28
S(g)	S^{-2}	+ 3.44

Sources: H^{-1}: Pitzer (19), p. 418. O^{-2}, S^{-2}: Sherman (23).
C^{-4}: computed by the writer.

Table 14

Bond Lengths and Bond Angles

Molecule	Bond Lengths in Angstroms	Bond Angles in Degrees
CH_4	C-H: 1.091	< HCH: 109.5
C_2H_6	C-H: 1.102 C-C: 1.543	< HCH: 109.3
C_3H_8	C-H: 1.09 C-C: 1.54 $\pm$ 0.02	< HCH: 109.5 < CCC: 111.5 $\pm$ 3
C_6H_6	C-H: 1.084 $\pm$ 0.006 C-C: 1.397 $\pm$ 0.001	< CCC: 120
C_2H_4	C-H: 1.071 $\pm$ 0.01 C-C: 1.353 $\pm$ 0.01	< HCH: 119.9 $\pm$ 0.5
C_2H_2	C-H: 1.059 C-C: 1.202	
C-C	C-C: 1.545	
CO_2	C-O: 1.162 $\pm$ 0.010 O-O: 2.310 $\pm$ 0.020	
H_2O	O-H: 0.958	< HOH: 104.45
H_2S	S-H: 1.3455	< HSH: 93.3
NH_3	N-H: 1.008 $\pm$ 0.004	< HNH: 107.3 $\pm$ 0.2
B_2H_6	(See Fig. 7, p. 50, for bond lengths and angles)	

Source: Sutton (24).

APPENDIX C

COMPUTATION OF THE NEGATIVE IONIZATION ENERGY OF CARBON

The negative ionization energy of carbon, computed from methane, is shown below:

Table 15

Computation of the Negative Ionization Energy of Carbon from Methane

Reaction		ΔH	
$C(s) + 2H_2(g) = CH_4(g)$	$+ \Delta H_1$	- 0.78	(1)
$C(s) = C(g)$	$+ \Delta H_2$	+ 5.98	(2)
$C(g) + 4\ e = C^{-4}(g)$	$+ \Delta H_3$	--	(3)
$2H_2(g) = 4H(g)$	$+ \Delta H_4$	+ 9.04	(4)
$4H(g) = 4H(g)^{+1} + 4\ e$	$+ \Delta H_5$	+54.40	(5)
$C^{-4}(g) + 4H^{+1}(g) = CH_4(g)$	$+ \Delta H_6$	--	(6)

The combination of reactions 2 through 6 yields reaction 7:

$$C(s) + 2H_2(g) = CH_4(g) + \sum_{i=2}^{6} \Delta H_i \qquad (7)$$

Reaction 7 is equivalent to reaction 1, so that

$$\Delta H_1 = \sum_{i=2}^{6} \Delta H_i \ . \qquad (8)$$

If the electrostatic energy, -162.67 eV, is substituted for ΔH_6 , equation (8) may be solved directly for ΔH_3 :

$$\Delta H_3 = -0.78 -(5.98 +9.04 +54.40 -162.67)$$

$$\Delta H_3 = +92.47 \text{ eV}.$$

Table 16 shows the negative ionization energy of carbon as computed from methane, ethane, propane, benzene, and ethylene. The negative ionization energy per carbon atom is denoted by U.

Table 16

Negative Ionization Energies of Carbon

Molecule	Charges	ΔE	U
CH_4	$C^{-4}H_4^{+1}$	-162.67	+92.47
C_2H_6	$C^{-4}H_3^{+1}C^{+4}H_3^{-1}$	-304.72	+91.70
C_3H_8	$C^{-4}H_3^{+1}C^{+4}H_2^{-1}C^{-4}H_3^{+1}$	-450.57	+91.95
C_3H_8	$C^{+4}H_3^{-1}C^{-4}H_2^{+1}C^{+4}H_3^{-1}$	-450.57	+94.63
C_6H_6		-809.64	+92.83
C_2H_4	$C^{-4}H_2^{+1}C^{+4}H_2^{-1}$	-281.71	+87.51

The average negative ionization energy of carbon computed from these molecules is equal to +91.85 eV per carbon atom.

APPENDIX D

ELECTROSTATIC ENERGIES OF MOLECULES

Tables 17 through 32 show the calculations of the electrostatic energies. The distances between the atoms were, for the most part, computed by the use of the distance formula. It was, therefore, necessary to determine the spatial coordinates of the atoms of most of the molecules. In some cases a sketch of the molecule is given and the atoms are numbered to identify them with the coordinates.

The computations of the electrostatic energies are presented in tabular form and all the details are shown. The designation of "ions" in the first column means the pair of ions between which the electrostatic energy is computed. The number of such pairs of ions is designated by n. Q_1 and Q_2 represent the charges on the first atom and second atom, respectively. The distance between the two atoms is denoted by R.

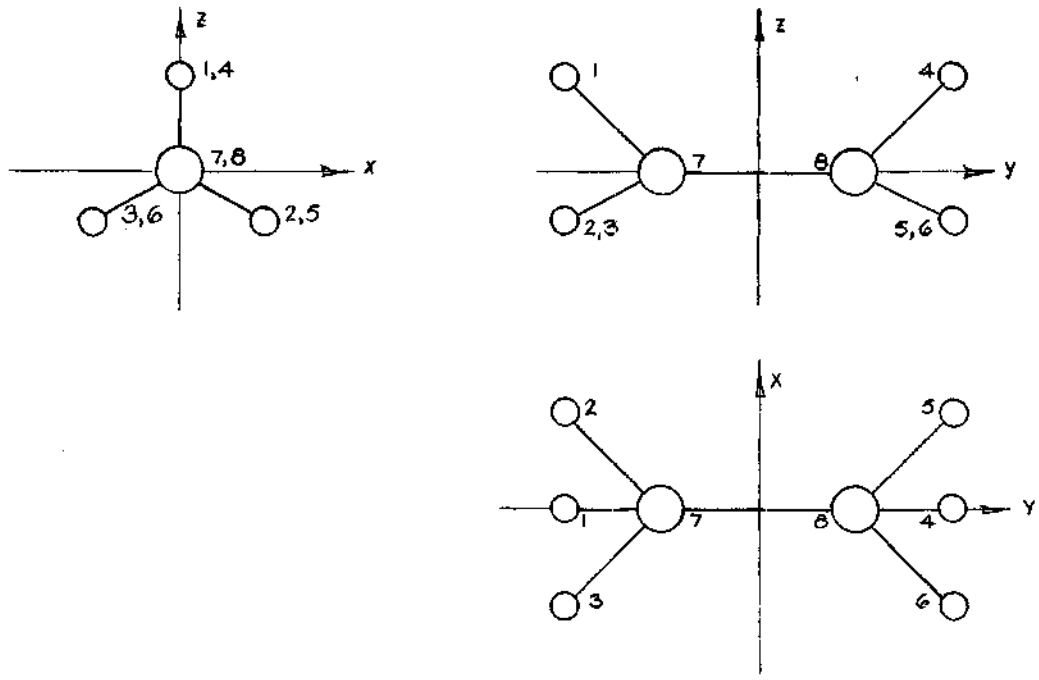


Figure 3. Ethane.

Table 17. Coordinates of the Atoms in Ethane.

Atom	x	y	z
1	0	-1.142	+1.038
2	+0.899	-1.142	-0.519
3	-0.899	-1.142	-0.519
4	0	+1.142	+1.038
5	+0.899	+1.142	-0.519
6	-0.899	+1.142	-0.519
7	0	-0.772	0
8	0	+0.772	0

Table 18

Electrostatic Energy of Ethane

Ions	n	Q_1Q_2	nQ_1Q_2	R	$nQ_1Q_2R^{-1}$
1-2	6	+ 1	+ 6	1.798	+ 3.3370
1-4	3	- 1	- 3	2.284	- 1.3135
1-5	6	- 1	- 6	2.907	- 2.0640
1-7	6	- 4	-24	1.102	-21.7786
1-8	6	+ 4	+24	2.177	+11.0243
7-8	1	-16	-16	1.543	-10.3694

$$\Sigma nQ_1Q_2R^{-1} = -21.1642$$

$$\Delta E = (14.398)(-21.1642)$$

$$\Delta E = -304.72 \text{ eV}$$

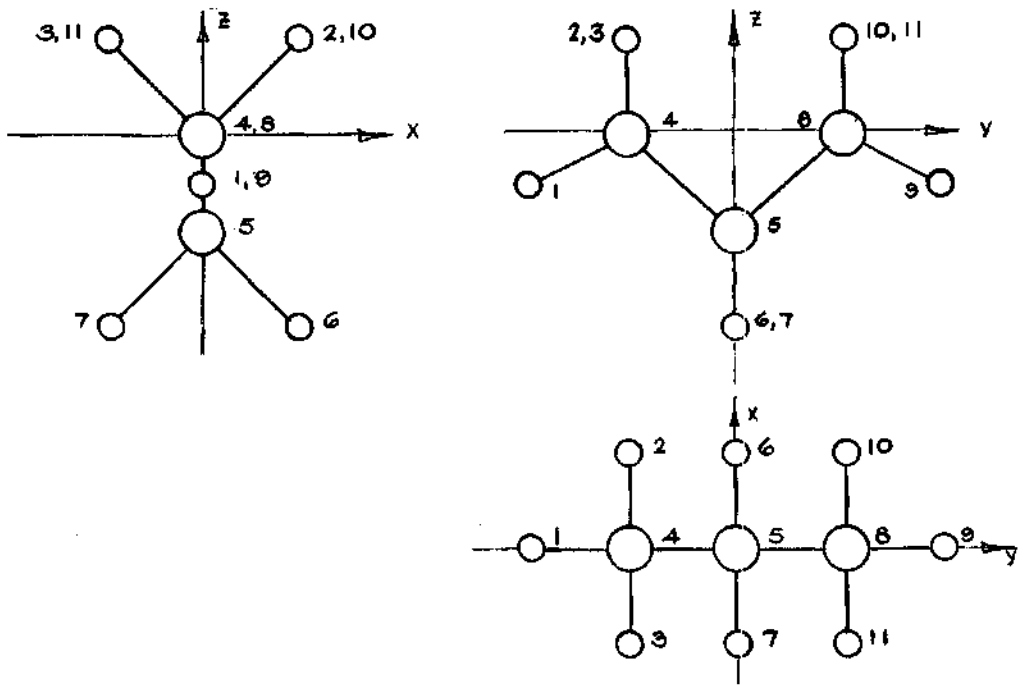


Figure 4. Propane

Table 19. Coordinates of the Atoms in Propane.

Atom	x	y	z
1	0	-2.15	-0.64
2	+0.89	-1.27	+0.62
3	-0.89	-1.27	+0.62
4	0	-1.27	0
5	0	0	-0.87
6	+0.89	0	-1.50
7	-0.89	0	-1.50
8	0	+1.27	0
9	0	+2.15	-0.64
10	+0.89	+1.27	+0.62
11	-0.89	+1.27	+0.62

Table 20

Electrostatic Energy of Propane

Ions	n	Q_1Q_2	nQ_1Q_2	R	$nQ_1Q_2R^{-1}$
1-2	7	+ 1	+ 7	1.78	+ 3.933
1-4	8	- 4	-32	1.09	-29.358
1-5	6	+ 4	+24	2.16	+11.111
1-7	4	- 1	- 4	2.48	- 1.613
1-8	2	- 4	- 8	3.48	- 2.299
1-9	1	+ 1	+ 1	4.30	+ 0.233
1-10	4	+ 1	+ 4	3.75	+ 1.067
2-6	4	- 1	- 4	2.47	- 1.619
2-7	4	- 1	- 4	3.05	- 1.311
2-8	4	- 4	-16	2.76	- 5.797
2-10	2	+ 1	+ 2	2.54	+ 0.787
2-11	2	+ 1	+ 2	3.10	+ 0.645
4-5	2	-16	-32	1.54	-20.779
4-6	4	+ 4	+16	2.16	+ 7.407
4-8	1	+16	+16	2.54	+ 6.299

$$\Sigma nQ_1Q_2R^{-1} = -31.294$$

$$\Delta E = (14.398)(-31.294)$$

$$\Delta E = -450.57 \text{ eV.}$$

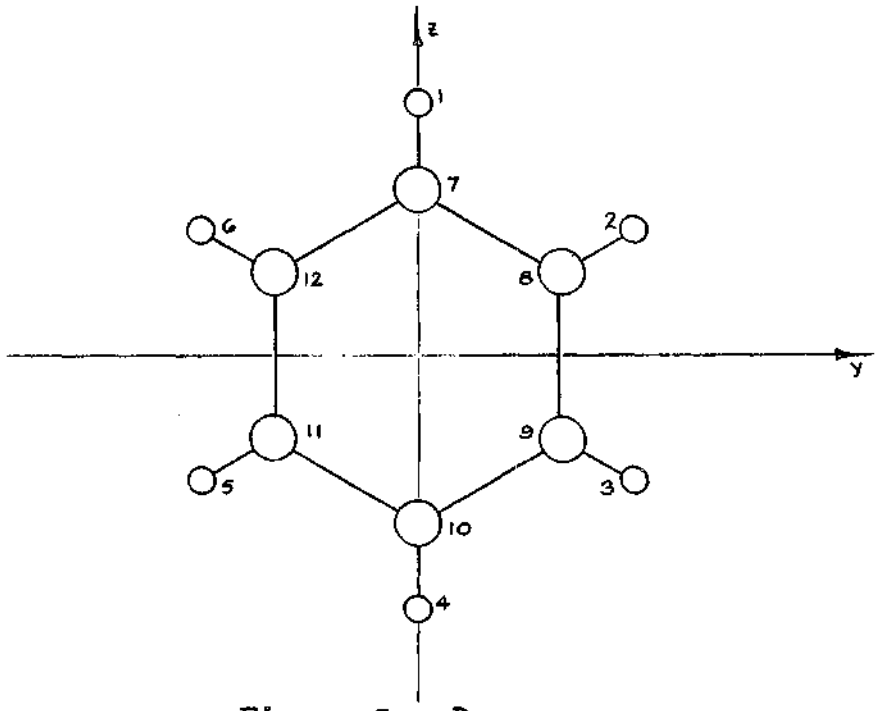


Figure 5. Benzene.

Table 21. Coordinates of the Atoms in Benzene.

Atom	y	z
1	0	+2.481
2	+2.149	+1.241
3	+2.149	-1.241
4	0	-2.481
5	-2.149	-1.241
6	-2.149	+1.241
7	0	+1.397
8	+1.210	+0.699
9	+1.210	-0.699
10	0	-1.397
11	-1.210	-0.699
12	-1.210	+0.699

Table 22

Electrostatic Energy of Benzene

Ions	n	Q_1Q_2	nQ_1Q_2	R	$nQ_1Q_2R^{-1}$
1-2	6	- 1	- 6	2.481	- 2.4184
1-3	6	+ 1	+ 6	4.298	+ 1.3960
1-4	6	- 1	- 6	4.962	- 1.2092
1-7	6	- 4	-24	1.084	-22.1402
1-8	12	+ 4	+48	2.154	+22.2841
1-9	12	- 4	-48	3.403	-14.1052
1-10	6	+ 4	+24	3.878	+ 6.1888
7-8	6	-16	-96	1.397	-68.7187
7-9	6	+16	+96	2.420	+39.6694
7-10	3	-16	-48	2.794	-17.1797

$$\Sigma nQ_1Q_2R^{-1} = -56.2331$$

$$\Delta E = (14.398)(-56.2331)$$

$$\Delta E = -809.64 \text{ eV.}$$

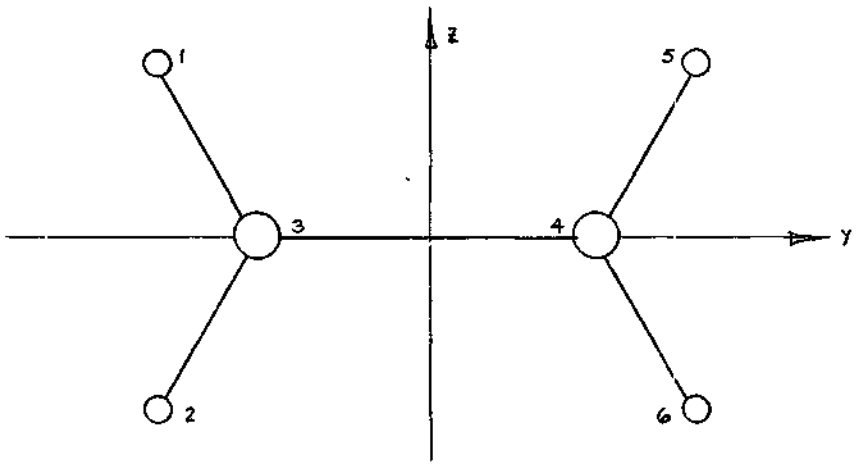


Figure 6. Ethylene.

Table 23. Coordinates of the Atoms in Ethylene.

Atom	y	z
1	-1.214	+0.926
2	-1.214	-0.926
3	-0.677	0
4	+0.677	0
5	+1.214	+0.926
6	+1.214	-0.926

Table 24

Electrostatic Energy of Ethylene

Ions	n	Q_1Q_2	nQ_1Q_2	R	$nQ_1Q_2R^{-1}$
1-2	2	+ 1	+ 2	1.852	+ 1.0799
1-3	4	- 4	-16	1.071	-14.9393
1-4	4	+ 4	+16	2.106	+ 7.5973
1-5	2	- 1	- 2	2.428	- 0.8237
1-6	2	- 1	- 2	3.054	- 0.6549
3-4	1	-16	-16	1.353	-11.8256

$$\Sigma nQ_1Q_2R^{-1} = -19.5663$$

$$\Delta E = (14.398)(-19.5663)$$

$$\Delta E = -281.71 \text{ eV.}$$

Table 25

Electrostatic Energy of Acetylene

Ions	n	Q_1Q_2	nQ_1Q_2	R	$nQ_1Q_2R^{-1}$
1-3	2	- 4	- 8	1.059	- 7.5543
3-4	1	-16	-16	1.202	-13.3111
1-4	2	+ 4	+ 8	2.261	+ 3.5383
1-2	1	- 1	- 1	3.320	-0.3012

$$\Sigma nQ_1Q_2R^{-1} = -17.6283$$

$$\Delta E = (14.398)(-17.6283)$$

$$\Delta E = -253.81 \text{ eV.}$$

Table 26

Electrostatic Energy of Carbon Dioxide

Ions	n	Q_1Q_2	nQ_1Q_2	R	$nQ_1Q_2R^{-1}$
C-O	2	-8	-16	1.162	-13.7694
O-O	1	+4	+ 4	2.310	+ 1.7316

$$\Sigma nQ_1Q_2R^{-1} = -12.0378$$

$$\Delta E = (14.398)(-12.0378)$$

$$\Delta E = -173.32 \text{ eV.}$$

Table 27

Electrostatic Energy of Water

Ions	n	Q_1Q_2	nQ_1Q_2	R	$nQ_1Q_2R^{-1}$
O-H	2	-2	-4	0.958	-4.1754
H-H	1	+1	+1	1.516	+0.6596

$$\Sigma nQ_1Q_2R^{-1} = -3.5158$$

$$\Delta E = (14.398)(-3.5158)$$

$$\Delta E = -50.62 \text{ eV.}$$

Table 28

Electrostatic Energy of Hydrogen Sulfide

Ions	n	Q_1Q_2	nQ_1Q_2	R	$nQ_1Q_2R^{-1}$
H-S	2	-2	-4	1.346	-2.9718
H-H	1	+1	+1	1.957	+0.5110

$$\Sigma nQ_1Q_2R^{-1} = -2.4608$$

$$\Delta E = (14.398)(-2.4608)$$

$$\Delta E = -35.43 \text{ eV.}$$

Table 29

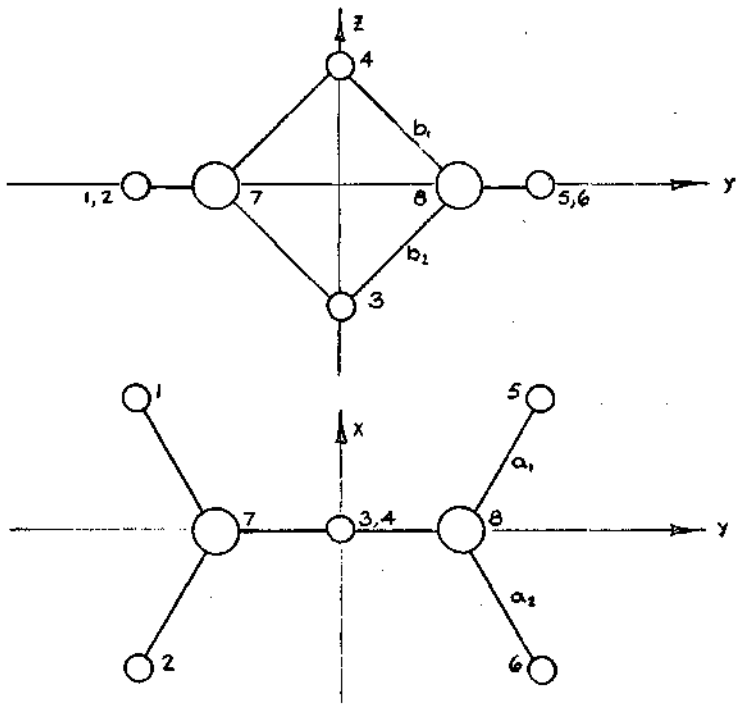
Electrostatic Energy of Ammonia

Ions	n	Q_1Q_2	nQ_1Q_2	R	$nQ_1Q_2R^{-1}$
N-H	3	-3	-9	1.008	-8.9286
H-H	3	+1	+3	1.623	+1.8484

$$\Sigma nQ_1Q_2R^{-1} = -7.0802$$

$$\Delta E = (14.398)(-7.0802)$$

$$\Delta E = -101.94 \text{ eV.}$$



$a_1 = a_2 = 1.187 \pm 0.03$ A B-B = 1.770 ± 0.013 A

$b_1 = b_2 = 1.334 \pm 0.027$A $< a_1a_2 = 121.5 \pm 7.5^{\circ}$

Figure 7. Diborane

Table 30. Coordinates of the Atoms in Diborane.

Atom	x	y	z
1	+1.036	-1.465	0
2	-1.036	-1.465	0
3	0	0	-0.998
4	0	0	+0.998
5	+1.036	+1.465	0
6	-1.036	+1.465	0
7	0	-0.885	0
8	0	+0.885	0

Table 31

Electrostatic Energy of Diborane

Ions	n	Q_1Q_2	nQ_1Q_2	R	$nQ_1Q_2R^{-1}$
1-2	2	+1	+ 2	2.072	+ 0.9653
1-3	8	+1	+ 8	2.053	+ 3.8967
1-5	2	+1	+ 2	2.930	+ 0.6826
1-6	2	+1	+ 2	3.589	+ 0.5573
1-7	4	-3	-12	1.187	-10.1095
1-8	4	-3	-12	2.568	- 4.6729
3-4	1	+1	+ 1	1.996	+ 0.5010
3-7	4	-3	-12	1.334	- 8.9955
7-8	1	+9	+ 9	1.770	+ 5.0847

$$\Sigma nQ_1Q_2R^{-1} = -12.0903$$

$$\Delta E = (14.398)(-12.0903)$$

$$\Delta E = -174.07 \text{ eV.}$$

Table 32

Electrostatic Energy of the Diamond Lattice

Ions	n	Q_1Q_2	nQ_1Q_2	R	$nQ_1Q_2R^{-1}$
C-C	1	-16	-16	1.545	-10.3560

$$\Delta E = (1.638)(14.398)(-10.3560)$$

$$\Delta E = -244.23 \text{ eV.}$$

The quantity 1.638 is Madelung's constant for sphalerite and the quantity -244.23 eV is the electrostatic energy of the pair of carbon ions in the diamond lattice.

APPENDIX E

THERMOCHEMICAL ENERGIES OF MOLECULES

Tables 33 through 48 show the computation of the thermochemical energies of the molecules. The full details are given for methane with an explanation of each of the steps in the computation. Since the computation of the thermochemical energies for the other molecules is almost identical to that of methane, only the steps in the calculation are shown.

Table 33

Thermochemical Energy of Methane

Reaction		ΔH	
$C(s) + 2H_2(g) = CH_4(g)$	$+\Delta H_1$	- 0.78	(1)
$C(s) = C(g)$	$+\Delta H_2$	+ 5.98	(2)
$C(g) + 4\ e = C^{-4}(g)$	$+\Delta H_3$	+91.85	(3)
$2H_2(g) = 4H(g)$	$+\Delta H_4$	+ 9.04	(4)
$4H(g) = 4H^{+1}(g) + 4\ e$	$+\Delta H_5$	+54.40	(5)
$C^{-4}(g) + 4H^{+1}(g) = CH_4(g)$	$+\Delta H_6$		(6)

The combination of reactions 2 through 6 yields reaction 7:

$$C(s) + 2H_2(g) = CH_4(g) + \sum_{i=2}^{6} \Delta H_i \qquad (7)$$

By comparing reaction 1 with reaction 7, it may be inferred that

$$\Delta H_1 = \sum_{i=2}^{6} \Delta H_i . \qquad (8)$$

Equation 8 may be solved directly for ΔH_6 :

$$\Delta H_6 = -0.78 - (5.98 + 91.85 + 9.04 + 54.40)$$

$$\Delta H_6 = -162.05 \text{ eV}.$$

Table 34

Thermochemical Energy of Ethane

Reaction		ΔH	
$2C(s) + 3H_2(g) = C_2H_6(g)$	$+\Delta H_1$	- 0.88	(1)
$2C(s) = 2C(g)$	$+\Delta H_2$	+ 11.96	(2)
$C(g) + 4\ e = C^{-4}(g)$	$+\Delta H_3$	+ 91.85	(3)
$C(g) = C^{+4}(g) + 4\ e$	$+\Delta H_4$	+147.98	(4)
$3H_2(g) = 6\ H(g)$	$+\Delta H_5$	+ 13.56	(5)
$3H(g) + 3\ e = 3H^{-1}(g)$	$+\Delta H_6$	- 2.16	(6)
$3H(g) = 3H^{+1}(g) + 3\ e$	$+\Delta H_7$	+ 40.80	(7)
$C^{+4}(g)+C^{-4}(g)+3H^{+1}(g)+3H^{-1}(g)$ $= C_2H_6(g)$	$+\Delta H_8$		(8)

$$2C(g) + 3H_2(g) = C_2H_6(g) + \sum_{i=2}^{8} \Delta H_i$$

$$\Delta H_1 = \sum_{i=2}^{8} \Delta H_i$$

$$\Delta H_8 = -0.88 - (11.96 + 91.85 + 147.98 + 13.56 + 40.80 - 2.16)$$

$$\Delta H_8 = -304.87 \text{ eV.}$$

Table 35

Thermochemical Energy of Propane with Two Negative Carbon Ions

Reaction		ΔH	
$3C(s) + 4H_2(g) = C_3H_8(g)$	$+\Delta H_1$	- 1.08	(1)
$3C(s) = 3C(g)$	$+\Delta H_2$	+ 17.94	(2)
$2C(g) + 8\ e = 2C^{-4}(g)$	$+\Delta H_3$	+183.70	(3)
$C(g) = C^{+4}(g) + 4\ e$	$+\Delta H_4$	+147.98	(4)
$4H_2(g) = 8H(g)$	$+\Delta H_5$	+ 18.08	(5)
$6H(g) = 6H^{+1}(g) + 6\ e$	$+\Delta H_6$	+ 81.60	(6)
$2H(g) + 2\ e = 2H^{-1}(g)$	$+\Delta H_7$	- 1.44	(7)
$2C^{-4}(g)+C^{+4}(g)+6H^{+1}(g)+2H^{-1}(g) = C_3H_8(g)$	$+\Delta H_8$		(8)

$$3C(s) + 4H_2(g) = C_3H_8(g) + \sum_{i=2}^{8} \Delta H_i$$

$$\Delta H_1 = \sum_{i=2}^{8} \Delta H_i$$

$$\Delta H_8 = -1.08 - (17.94 + 183.70 + 147.98 + 18.08 + 81.61 - 1.44)$$

$$\Delta H_8 = -448.94 \text{ eV}.$$

Table 36

Thermochemical Energy of Propane with One Negative Carbon Ion

Reaction		ΔH	
$3C(s) + 4H_2(g) = C_3H_8(g)$	$+\Delta H_1$	- 1.08	(1)
$3C(s) = 3C(g)$	$+\Delta H_2$	+ 17.94	(2)
$C(g) + 4\ e = C^{-4}(g)$	$+\Delta H_3$	+ 91.85	(3)
$2C(g) = 2C^{+4}(g) + 8\ e$	$+\Delta H_4$	+295.96	(4)
$4H_2(g) = 8H(g)$	$+\Delta H_5$	+ 18.08	(5)
$2H(g) = 2H^{+1}(g) + 2\ e$	$+\Delta H_6$	+ 27.20	(6)
$6H(g) + 6\ e = 6H^{-1}(g)$	$+\Delta H_7$	- 4.32	(7)
$C^{-4}(g)+2C^{+4}(g)+2H^{+1}(g)+6H^{-1}(g)$ $= C_3H_8(g)$	$+\Delta H_8$		(8)

$$3C(s) + 4H_2(g) = C_3H_8(g) + \sum_{i=2}^{8} \Delta H_i$$

$$\Delta H_1 = \sum_{i=2}^{8} \Delta H_i$$

$$\Delta H_8 = -1.08 - (17.94 + 91.85 + 295.96 + 18.08 + 27.20 - 4.32)$$

$$\Delta H_8 = -447.79 \text{ eV.}$$

Table 37

Thermochemical Energy of Benzene with Three Negative Carbon Ions

Reaction		ΔH	
$6C(s) + 3H_2(g) = C_6H_6(g)$	$+\Delta H_1$	+ 0.86	(1)
$6C(s) = 6C(g)$	$+\Delta H_2$	+ 35.88	(2)
$3C(g) + 12\ e = 3C^{-4}(g)$	$+\Delta H_3$	+275.55	(3)
$3C(g) = 3C^{+4}(g) + 12\ e$	$+\Delta H_4$	+443.94	(4)
$3H_2(g) = 6H(g)$	$+\Delta H_5$	+ 13.56	(5)
$3H(g) = 3H^{+1}(g) + 3\ e$	$+\Delta H_6$	+ 40.80	(6)
$3H(g) + 3\ e = 3H^{-1}(g)$	$+\Delta H_7$	- 2.16	(7)
$3C^{+4}(g)+3C^{-4}(g)+3H^{+1}(g)+3H^{-1}(g) = C_6H_6(g)$	$+\Delta H_8$		(8)

$$6C(s) + 3H_2(g) = C_6H_6(g) + \sum_{i=2}^{8} \Delta H_i$$

$$\Delta H_1 = \sum_{i=2}^{8} \Delta H_i$$

$$\Delta H_8 = +0.86 - (35.88 + 275.55 + 443.94 + 13.56 + 40.80 - 2.16)$$

$$\Delta H_8 = -806.71 \text{ eV.}$$

Table 38

Thermochemical Energy of Ethylene with One Negative Carbon Ion

Reaction		ΔH	
$2C(s) + 2H_2(g) = C_2H_4(g)$	$+\Delta H_1$	+ 0.54	(1)
$2C(s) = 2C(g)$	$+\Delta H_2$	+ 11.96	(2)
$C(g) + 4\ e = C^{-4}(g)$	$+\Delta H_3$	+ 91.85	(3)
$C(g) = C^{+4}(g) + 4\ e$	$+\Delta H_4$	+147.98	(4)
$2H_2(g) = 4H(g)$	$+\Delta H_5$	+ 9.04	(5)
$2H(g) = 2H^{+1}(g) + 2\ e$	$+\Delta H_6$	+ 27.20	(6)
$2H(g) + 2\ e = 2H^{-1}(g)$	$+\Delta H_7$	- 1.44	(7)
$C^{+4}(g)+C^{-4}(g)+2H^{+1}(g)+2H^{-1}(g) = C_2H_4(g)$	$+\Delta H_8$		(8)

$$2C(s) + 2H_2(g) = C_2H_4(g) + \sum_{i=2}^{8} \Delta H_i$$

$$\Delta H_1 = \sum_{i=2}^{8} \Delta H_i$$

$$\Delta H_8 = +0.54 - (11.96 + 91.85 + 147.98 + 9.04 + 27.20 - 1.44)$$

$$\Delta H_8 = -286.05 \text{ eV.}$$

Table 39

Thermochemical Energy of Acetylene with One Negative Carbon Ion

Reaction		ΔH	
$2C(s) + H_2(g) = C_2H_2(g)$	$+\Delta H_1$	+ 2.35	(1)
$2C(s) = 2C(g)$	$+\Delta H_2$	+ 11.96	(2)
$C(g) + 4\ e = C^{-4}(g)$	$+\Delta H_3$	+ 91.85	(3)
$C(g) = C^{+4}(g) + 4\ e$	$+\Delta H_4$	+147.98	(4)
$H_2(g) = 2H(g)$	$+\Delta H_5$	+ 4.52	(5)
$H(g) = H^{+1}(g) + e$	$+\Delta H_6$	+ 13.60	(6)
$H(g) + e = H^{-1}(g)$	$+\Delta H_7$	- 0.72	(7)
$C^{+4}(g)+C^{-4}(g)+H^{+1}(g)+H^{-1}(g)$ $= C_2H_2(g)$	$+\Delta H_8$		(8)

$$2C(s)+H_2(g) = C_2H_2(g) + \sum_{i=2}^{8} \Delta H_i$$

$$\Delta H_1 = \sum_{i=2}^{8} \Delta H_i$$

$$\Delta H_8 = +2.35 - (11.96 + 91.85 + 147.98 + 4.52 + 13.60 - 0.72)$$

$$\Delta H_8 = -266.84 \text{ eV}.$$

Table 40

Thermochemical Energy of Carbon Dioxide with a Negative Carbon Ion

Reaction		ΔH	
$C(s) + O_2(g) = CO_2(g)$	$+\Delta H_1$	- 4.08	(1)
$C(s) = C(g)$	$+\Delta H_2$	+ 5.98	(2)
$C(g) + 4\ e = C^{-4}(g)$	$+\Delta H_3$	+91.85	(3)
$O_2(g) = 2\ O(g)$	$+\Delta H_4$	+ 5.13	(4)
$2\ O(g) = 2\ O^{+2}(g) + 4\ e$	$+\Delta H_5$	+97.52	(5)
$C^{-4}(g) + 2\ O^{+2}(g) = CO_2(g)$	$+\Delta H_6$		(6)

$$C(s) + O_2(g) = CO_2(g) + \sum_{i=2}^{6} \Delta H_i$$

$$\Delta H_1 = \sum_{i=2}^{6} \Delta H_i$$

$$\Delta H_6 = -4.08 - (5.98 + 91.85 + 5.13 + 97.52)$$

$$\Delta H_6 = -204.56 \text{ eV.}$$

Table 41

Thermochemical Energy of the Diamond Lattice

Reaction		ΔH	
$2C(g) = 2C(\text{graphite})$	$+\Delta H_1$	- 11.96	(1)
$2C(\text{graphite}) = 2C(\text{diamond})$	$+\Delta H_2$	+ 0.04	(2)
$C(g) + 4\ e = C^{-4}(g)$	$+\Delta H_3$	+ 91.85	(3)
$C(g) = C^{+4}(g) + 4\ e$	$+\Delta H_4$	+147.98	(4)
$C^{-4}(g)+C^{+4}(g) = 2C(\text{diamond})$	$+\Delta H_5$		(5)

$$2C(g) = 2C(\text{diamond}) + \Delta H_1 + \Delta H_2$$

$$2C(g) = 2C(\text{diamond}) + \Delta H_3 + \Delta H_4 + \Delta H_5$$

$$\Delta H_1 + \Delta H_2 = \Delta H_3 + \Delta H_4 + \Delta H_5$$

$$\Delta H_5 = -11.96 + 0.04 - (91.85 + 147.98)$$

$$\Delta H_5 = -251.75 \text{ eV}.$$

Table 42

Thermochemical Energy of Carbon Dioxide with a Positive Carbon Ion

Reaction		ΔH	
$C(s) + O_2(g) = CO_2(g)$	$+\Delta H_1$	- 4.08	(1)
$C(s) = C(g)$	$+\Delta H_2$	+ 5.98	(2)
$C(g) = C^{+4}(g) + 4\ e$	$+\Delta H_3$	+147.98	(3)
$O_2(g) = 2\ O(g)$	$+\Delta H_4$	+ 5.13	(4)
$2\ O(g) + 4\ e = 2\ O^{-2}(g)$	$+\Delta H_5$	+ 14.56	(5)
$C^{+4}(g) + 2\ O^{-2}(g) = CO_2(g)$	$+\Delta H_6$		(6)

$$C(s) + O_2(g) = CO_2(g) + \sum_{i=2}^{6} \Delta H_i$$

$$\Delta H_1 = \sum_{i=2}^{6} \Delta H_i$$

$$\Delta H_6 = -4.08 - (5.98 + 147.98 + 5.13 + 14.56)$$

$$\Delta H_6 = -177.73 \text{ eV.}$$

Table 43

Thermochemical Energy of Water with a Positive Oxygen Ion

Reaction		ΔH	
$H_2(g) + \frac{1}{2}O_2(g) = H_2O(g)$	$+\Delta H_1$	- 2.51	(1)
$\frac{1}{2}O_2(g) = O(g)$	$+\Delta H_2$	+ 2.57	(2)
$O(g) = O^{+2}(g) + 2\ e$	$+\Delta H_3$	+48.76	(3)
$H_2(g) = 2\ H(g)$	$+\Delta H_4$	+ 4.52	(4)
$2H(g) + 2\ e = 2H^{-1}(g)$	$+\Delta H_5$	- 1.44	(5)
$2H^{-1}(g) + O^{+2}(g) = H_2O(g)$	$+\Delta H_6$		(6)

$$H_2(g) + \tfrac{1}{2}O_2(g) = H_2O(g) + \sum_{i=2}^{6} \Delta H_i$$

$$\Delta H_1 = \sum_{i=2}^{6} \Delta H_i$$

$$\Delta H_6 = -2.51 - (2.57 + 48.76 + 4.52 - 1.44)$$

$$\Delta H_6 = -56.92 \text{ eV.}$$

Table 44

Thermochemical Energy of Water with a Negative Oxygen Ion

Reaction		ΔH	
$H_2(g) + \frac{1}{2}O_2(g) = H_2O(g)$	$+\Delta H_1$	- 2.51	(1)
$\frac{1}{2}O_2(g) = O(g)$	$+\Delta H_2$	+ 2.57	(2)
$O(g) + 2\ e = O^{-2}(g)$	$+\Delta H_3$	+ 7.28	(3)
$H_2(g) = 2H(g)$	$+\Delta H_4$	+ 4.52	(4)
$2H(g) = 2H^{+1}(g) + 2\ e$	$+\Delta H_5$	+27.20	(5)
$2H^{+1}(g) + O^{-2}(g) = H_2O(g)$	$+\Delta H_6$		(6)

$$H_2(g) + \tfrac{1}{2}O_2(g) = H_2O(g) + \sum_{i=2}^{6} \Delta H_i$$

$$\Delta H_1 = \sum_{i=2}^{6} \Delta H_i$$

$$\Delta H_6 = -2.51 - (2.57 + 7.28 + 4.52 + 27.20)$$

$$\Delta H_6 = -44.08 \text{ eV.}$$

Table 45

Thermochemical Energy of Hydrogen Sulfide with a Positive Sulfur Ion

Reaction		ΔH	
$S(s) + H_2(g) = H_2S(g)$	$+\Delta H_1$	- 0.21	(1)
$S(s) = S(g)$	$+\Delta H_2$	+ 2.87	(2)
$S(g) = S^{+2}(g) + 2\ e$	$+\Delta H_3$	+33.76	(3)
$H_2(g) = 2H(g)$	$+\Delta H_4$	+ 4.52	(4)
$2H(g) + 2\ e = 2H^{-1}(g)$	$+\Delta H_5$	- 1.44	(5)
$S^{+2}(g)+2H^{-1}(g) = H_2S(g)$	$+\Delta H_6$		(6)

$$S(s) + H_2(g) = H_2S(g) + \sum_{i=2}^{6} \Delta H_i$$

$$\Delta H_1 = \sum_{i=2}^{6} \Delta H_i$$

$$\Delta H_6 = -0.21 -(2.87 + 33.76 + 4.52 - 1.44)$$

$$\Delta H_6 = -39.92 \text{ eV}.$$

Table 46

Thermochemical Energy of Hydrogen Sulfide with a Negative Sulfur Ion

Reaction		ΔH	
$S(s) + H_2(g) = H_2S(g)$	$+\Delta H_1$	- 0.21	(1)
$S(s) = S(g)$	$+\Delta H_2$	+ 2.87	(2)
$S(g) + 2\ e = S^{-2}(g)$	$+\Delta H_3$	+ 3.44	(3)
$H_2(g) = 2H(g)$	$+\Delta H_4$	+ 4.52	(4)
$2H(g) = 2H^{+1}(g) + 2\ e$	$+\Delta H_5$	+27.20	(5)
$2H^{+1}(g)+S^{-2}(g) = H_2S(g)$	$+\Delta H_6$		(6)

$$S(s) + H_2(g) = H_2S(g) + \sum_{i=2}^{6} \Delta H_i$$

$$\Delta H_1 = \sum_{i=2}^{6} \Delta H_i$$

$$\Delta H_6 = -0.21 -(2.87 + 3.44 + 4.52 + 27.20)$$

$$\Delta H_6 = -41.84 \text{ eV.}$$

Table 47

Thermochemical Energy of Ammonia with a Positive Nitrogen Ion

Reaction		ΔH	
$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) = NH_3(g)$	$+\Delta H_1$	- 0.48	(1)
$\frac{1}{2}N_2(g) = N(g)$	$+\Delta H_2$	+ 3.71	(2)
$N(g) = N^{+3}(g) + 3\ e$	$+\Delta H_3$	+91.57	(3)
$\frac{3}{2}H_2(g) = 3H(g)$	$+\Delta H_4$	+ 6.78	(4)
$3H(g) + 3\ e = 3H^{-1}(g)$	$+\Delta H_5$	- 2.16	(5)
$N^{+3}(g)+3H^{-1}(g) = NH_3(g)$	$+\Delta H_6$		(6)

$$\tfrac{1}{2}N_2(g) + \tfrac{3}{2}H_2(g) = NH_3(g) + \sum_{i=2}^{6} \Delta H_i$$

$$\Delta H_1 = \sum_{i=2}^{6} \Delta H_i$$

$$\Delta H_6 = -0.48 - (3.71 + 91.57 + 6.78 - 2.16)$$

$$\Delta H_6 = -100.38 \text{ eV.}$$

Table 48

Thermochemical Energy of Diborane with Two Positive Boron Ions

Reaction		ΔH	
$2B(s) + 3H_2(g) = B_2H_6(g)$	$+\Delta H_1$	+ 0.33	(1)
$2B(s) = 2B(g)$	$+\Delta H_2$	+ 8.42	(2)
$2B(g) = 2B^{+3}(g) + 6\ e$	$+\Delta H_3$	+142.74	(3)
$3H_2(g) = 6H(g)$	$+\Delta H_4$	+ 13.56	(4)
$6H(g) + 6\ e = 6H^{-1}(g)$	$+\Delta H_5$	- 4.32	(5)
$2B^{+3}(g)+6H^{-1}(g) = B_2H_6(g)$	$+\Delta H_6$		(6)

$$2B(s) + 3H_2(g) = B_2H_6(g) + \sum_{i=2}^{6} \Delta H_i$$

$$\Delta H_1 = \sum_{i=2}^{6} \Delta H_i$$

$$\Delta H_6 = +0.33 - (8.42 + 142.74 + 13.56 - 4.32)$$

$$\Delta H_6 = -160.07 \text{ eV}$$

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